

METHOD FOR IMPROVING EFFERVESCENCY OF A DETERGENT PRODUCTFIELD OF THE INVENTION

The present invention relates generally to a detergent product, and particularly to a particulate or a non-particulate detergent product containing an aluminosilicate ion exchange material which serves not only as a builder but also as a means for improving the effervescency of the detergent product when the product is placed in an aqueous medium.

BACKGROUND OF THE INVENTION Non-particulate detergents are an attractive alternative to granular or particulate forms of detergents from the standpoint of simplifying the dosing of such detergents for automatic laundry or dishwashing machines. Non-particulate detergents are usually supplied in the form of bars, tablets or briquettes and they not only prevent spillage of the detergent composition but also eliminate the need for the consumer to estimate the correct dosage of the detergent composition per wash.

There is a desire by consumers to have non-particulate detergent products, such as detergent tablets, that are effervescent when placed in an aqueous washing medium. Typically effervescency is delivered by incorporating an acid and a carbonate form, for example, citric acid and sodium bicarbonate, in a detergent composition. However, this does not provide weight effective benefits to the detergent composition, such as improved building properties.

There has been thus a desire for a process to not only deliver effervescency but also provide a by product that is useful. Particularly, it has been desirable to have a process for improving both effervescency and building properties.

The present invention provides both of the aforementioned desirable features by providing a particulate or a non-particulate detergent product containing an aluminosilicate ion exchange material which serves not only as a builder but also as a means for improving the effervescency of the detergent product when the product is placed in an aqueous medium. The invention also provides a process for achieving the above objectives. The process involves taking an aluminosilicate ion exchange material, such as zeolite for example, and driving off the moisture from the zeolite so that its pores are substantially empty. Then, carbon dioxide or some other suitable gas is entrapped into the pores. When the zeolite is thrown into an aqueous wash medium, the carbon dioxide gas bubbles out, causing effervescency. The invention thus exploits the use of an aluminosilicate ion exchange material, such as zeolite, which is a useful builder and a useful effervescency delivering agent.

These and other objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following detailed description of the preferred embodiment and the appended claims.

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs by disclosing a method of using an aluminosilicate ion exchange material for delivering effervescency in a detergent product, a method for forming a laundry detergent product exhibiting a combination of effervescency and building properties, a laundry detergent product, and a method for laundering soiled clothes.

In one aspect of the present invention, a method of using an aluminosilicate ion exchange material for delivering effervescency in a detergent product comprises the steps of providing an aluminosilicate ion exchange material having pores. The method includes drying the aluminosilicate ion exchange material, entrapping a gas into the pores of the aluminosilicate ion exchange material, adding the aluminosilicate ion exchange material having gas entrapped therein to a detergent composition and forming a detergent product exhibiting effervescency when the detergent product is placed in an aqueous medium.

In another aspect of the present invention, a method for forming a laundry detergent product exhibiting a combination of effervescency and building properties, comprising the steps of providing an aluminosilicate ion exchange material having pores, entrapping a gas into the pores of the aluminosilicate ion exchange material, adding the aluminosilicate ion exchange material having gas entrapped therein to a laundry detergent composition, and forming a laundry detergent product exhibiting effervescency and building properties when the detergent product is placed in an aqueous medium.

In yet another aspect of the present invention, a laundry detergent product comprises a laundry detergent composition including a surfactant and a builder, wherein the builder is adapted to deliver a combination of building properties and effervescency properties to the laundry detergent composition. The builder includes an aluminosilicate ion exchange material of the formula; $Mm/n [(AlO_2)_m(SiO_2)_y] \cdot xH_2O$ where n is the valence of the cation M , x is the number of water molecules per unit cell, m and y are the total number of tetrahedra per unit cell, and y/m is 1 to 100, and wherein M is selected from the group consisting of sodium, potassium, magnesium, and calcium. The aluminosilicate ion exchange material has pores, and the aluminosilicate ion exchange material has a gas entrapped within

the pores. The detergent product exhibits effervescency when the detergent product is placed in an aqueous medium.

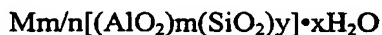
In still another aspect of the present invention, a method of laundering soiled clothes is disclosed. The method comprises the step of immersing the soiled clothes in an aqueous medium containing an effective amount of a laundry detergent product made by a method as recited above.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment of the present invention, a method of using an aluminosilicate ion exchange material for delivering effervescency in a detergent product comprises the steps of providing an aluminosilicate ion exchange material having pores.

Aluminosilicate material

The structural formula of an aluminosilicate material is based on the crystal unit cell, the smallest unit of structure represented by:



where n is the valence of the cation M, x is the number of water molecules per unit cell, m and y are the total number of tetrahedra per unit cell, and y/m is 1 to 100. Most preferably, y/m is 1 to 5. The cation M can be Group IA and Group IIA elements, such as sodium, potassium, magnesium, and calcium. The preferred aluminosilicate materials are zeolites. The most preferred zeolites are zeolite A, zeolite X, zeolite Y, zeolite P, zeolite MAP and mixtures thereof.

The aluminosilicate ion exchange materials used herein preferably have both a high calcium ion exchange capacity and a high exchange rate. Without intending to be limited by theory, it is believed that such high calcium ion exchange rate and capacity are a function of several interrelated factors which derive from the method by which the aluminosilicate ion exchange material is produced. In that regard, the aluminosilicate ion exchange materials used herein are preferably produced in accordance with Corkill et al, U.S. Patent No. 4,605,509 (Procter & Gamble), the disclosure of which is incorporated herein by reference.

Preferably, the aluminosilicate ion exchange material is in "sodium" form since the potassium and hydrogen forms of the instant aluminosilicate do not exhibit the as high of an exchange rate and capacity as provided by the sodium form. Additionally, the aluminosilicate ion exchange material preferably is in over dried form so as to facilitate production of crisp detergent agglomerates as described herein. The aluminosilicate ion exchange materials used herein preferably have particle size diameters which optimize their effectiveness as detergent

builders. The term "particle size diameter" as used herein represents the average particle size diameter of a given aluminosilicate ion exchange material as determined by conventional analytical techniques, such as microscopic determination and scanning electron microscope (SEM). The preferred particle size diameter of the aluminosilicate is from about 0.1 micron to about 10 microns, more preferably from about 0.5 microns to about 9 microns. Most preferably, the particle size diameter is from about 1 microns to about 8 microns.

In a preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula: $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$, wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. In the preferred embodiment, the aluminosilicate ion exchange material is zeolite and the zeolite acts as a builder.

In the preferred embodiment, the aluminosilicate ion exchange material has pores having a pore diameter in a range of from about 2 ANGSTROMS to about 12 ANGSTROMS. Further, desirably, the aluminosilicate ion exchange material has a total porosity of at least 25 %.

In the preferred embodiment, the method also includes drying the aluminosilicate ion exchange material. This is accomplished by heating the aluminosilicate ion exchange material to a temperature of at least 20 degrees C.

In the preferred embodiment, the method also includes entrapping a gas into the pores of the aluminosilicate ion exchange material. The preferred gas is carbon dioxide. The method also includes placing the aluminosilicate ion exchange material inside a pressureable container and entrapping the gas into the pores of the aluminosilicate ion exchange material at a gas pressure of at least 1 atmospheres.

In the preferred embodiment, the method also includes adding the aluminosilicate ion exchange material having gas entrapped therein to a detergent composition and forming a detergent product exhibiting effervescency when the detergent product is placed in an aqueous medium. The aluminosilicate ion exchange material having gas entrapped therein is added to the detergent composition in an amount in a range of from about 1 % to about 25 % by weight of the detergent composition.

In the preferred embodiment, the detergent composition is free of citric acid and bicarbonates.

The non-particulate detergent product

The detergent tablets can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry.

The detergent tablets provided can be made in any size or shape. Prior to compaction, the detergent particles may be surface treated with a flow aid according to the present invention. The detergent tablets provided may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). As used herein, the term "non-particulate detergent product" includes physical shapes such as tablets, blocks, bars and the like.

Coating for non-particulate detergent product

In one embodiment, the tablets are coated with a coating in order to provide mechanical strength and shock and chip resistance to the compressed tablet core. The tablets are coated with a coating that is substantially insoluble in water so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Further, the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dissolved under alkaline conditions, or is readily emulsified by surfactants. This avoids the deposition of undissolved particles or lumps of coating material on the laundry load. This may be important when the coating material is completely insoluble (for example less than 1 g/l) in water.

As defined herein "substantially insoluble" means having a very low solubility in water. This should be understood to mean having a solubility in water at 25°C of less than 20 g/L, preferably less than 5 g/l, and more preferably less than 1 g/l. Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials are fatty acids, adipic acid and C8-C13 dicarboxylic acids, fatty alcohols, diols, esters and ethers. Preferred fatty acids are those having a carbon chain length of from C12 to C22 and most preferably from C18 to C22. Preferred dicarboxylic acids are adipic acid (C6), suberic acid (C8), azelaic acid (C9), sebacic acid (C10), undecanedioic acid (C11), dodecanedioic acid (C12) and tridecanedioic acid (C13). Preferred fatty alcohols are those having a carbon chain length of from C12 to C22 and most preferably from C14 to

C18. Preferred diols are 1,2-octadecanediol and 1,2-hexadecanediol. Preferred esters are tristearin, tripalmitin, methylbehenate, ethylstearate. Preferred ethers are diethyleneglycol mono hexadecylether, diethyleneglycol mono octadecylether, diethyleneglycol mono tetradecylether, phenylether, ethyl naphtyl ether, 2 methoxynaphtalene, beta naphtyl methyl ether and glycerol monooctadecylether. Other preferred coating materials include dimethyl 2,2 propanol, 2 hexadecanol, 2 octadecanone, 2 hexadecanone, 2, 15 hexadecanedione and 2 hydroxybenzyl alcohol. The coating is a hydrophobic material having a melting point preferably of from 40 °C to 180 °C.

In the preferred embodiment, the coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material. In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40 °C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 180 °C are not practicable to use. Preferably, the materials melt in the range from 60 °C to 160 °C, more preferably from 70 °C to 120 °C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

Surfactants

Anionic Surfactant - The preferred anionic surfactants include C₁₁-C₁₈ alkyl benzene sulfonates (LAS) and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates (AS), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺) CH₃ and CH₃ (CH₂)_y(CHOSO₃⁻M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters.

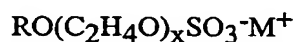
Generally speaking, anionic surfactants useful herein are disclosed in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin et al, issued December 30, 1975.

Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water-soluble salts of esters of α-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and n-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Other useful anionic surfactants herein are the alkyl polyethoxylate sulfates of the formula



wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 1 to about 15.

Other alkyl sulfate surfactants are the non-ethoxylated C₁₂₋₁₅ primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Nonionic Surfactant - Conventional nonionic and amphoteric surfactants include C₁₂-C₁₈ alkyl ethoxylates (AE) including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy). The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Examples of nonionic surfactants are described in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981.

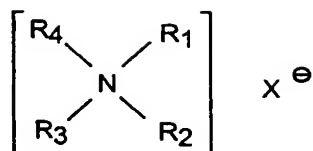
Examples of surfactants also include ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)_nOH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981. Other surfactants include ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol. Mixtures of anionic and nonionic surfactants are especially useful.

Other conventional useful surfactants are listed in standard texts, including polyhydroxy fatty acid amides, alkyl glucosides, polyalkyl glucosides, C₁₂-C₁₈ betaines and sulfobetaines (sultaines). Examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing.

Cationic Surfactants

One class of useful cationic surfactants are the mono alkyl quaternary ammonium surfactants although any cationic surfactant useful in detergent compositions are suitable for use herein.

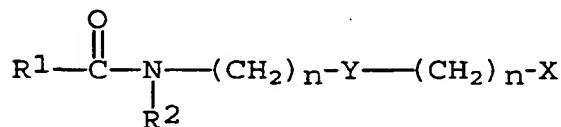
The cationic surfactants which can be used herein include quaternary ammonium surfactants of the formula:



wherein R_1 and R_2 are individually selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from about 2 to about 5; X is an anion; and (1) R_3 and R_4 are each a C_6 - C_{14} alkyl or (2) R_3 is a C_6 - C_{18} alkyl, and R_4 is selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} hydroxyalkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5.

Other useful quaternary ammonium surfactants are the chloride, bromide, and methylsulfate salts. Examples of desirable mono-long chain alkyl quaternary ammonium surfactants are those wherein R_1 , R_2 , and R_4 are each methyl and R_3 is a C_8 - C_{16} alkyl; or wherein R_3 is C_8 - C_{18} alkyl and R_1 , R_2 , and R_4 are selected from methyl and hydroxyalkyl moieties. Lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxy-ethylammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethyl-monohydroxyethylammonium methylsulfate, di- C_{12} - C_{14} alkyl dimethyl ammonium chloride, and mixtures thereof are also desirable. ADOGEN 412™, a lauryl trimethyl ammonium chloride commercially available from Witco, is also desirable. Other desirable surfactants are lauryl trimethyl ammonium chloride and myristyl trimethyl ammonium chloride.

Another group of suitable cationic surfactants are the alkanol amidal quaternary surfactants of the formula:



wherein R^1 can be C_{10} - C_{18} alkyl or a substituted or unsubstituted phenyl; R^2 can be a C_1 - C_4 alkyl, H, or $(EO)_y$, wherein y is from about 1 to about 5; Y is O or $-N(R^3)(R^4)$; R^3 can be H, C_1 - C_4 alkyl, or $(EO)_y$, wherein y is from about 1 to about 5; R^4 , if present, can be C_1 - C_4 alkyl or $(EO)_y$, wherein y is from about 1 to about 5; each n is independently selected from about 1 to about 6, preferably from about 2 to about 4; X is hydroxyl or

$-N(R^5)(R^6)(R^7)$, wherein R^5 , R^6 , R^7 are independently selected from C_{1-4} alkyl, H, or $(EO)_y$, wherein y is from about 1 to about 5.

Amine Oxide Surfactants - The compositions herein also contain amine oxide surfactants of the formula:



In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R' . R' is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When $x+y+z = 0$, R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When $x+y+z$ is different from 0, R^1 may be somewhat longer, having a chainlength in the range $C_{12}-C_{24}$. The general formula also encompasses amine oxides wherein $x+y+z = 0$, $R^1 = C_8-C_{18}$, R' is H and q is 0-2, preferably 2. These amine oxides are illustrated by C_{12-14} alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein $x+y+z$ is different from zero, specifically $x+y+z$ is from about 1 to about 10, R^1 is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y + z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Desirable amine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range $30^\circ C$ to $90^\circ C$. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Other desirable commercially available amine oxides are the solid, dihydrate ADMOX 16 and ADMOX 18, ADMOX 12 and especially ADMOX 14 from Ethyl Corp.

Other embodiments include dodecyldimethylamine oxide dihydrate, hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate,

hexadecyltris(ethyleneoxy)dimethyl-amine oxide, tetradecyldimethylamine oxide dihydrate, and mixtures thereof. Whereas in certain embodiments R' is H, there is some latitude with respect to having R' slightly larger than H. Alternate embodiments include wherein R' is CH₂OH, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

Enzymes

Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, and cellulases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01% to 1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered tradename ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade names ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Diosynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

The enzymes employed herein may be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species. See Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 4%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other

alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

Polymeric Soil Release Agent

Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Examples of polymeric soil release agents useful herein include U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink; U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.; European Patent Application 0 219 048, published April 22, 1987 by Kud, et al.; U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink; U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel. Commercially available soil release agents include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany). Also see U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink. Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating

agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent

Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Brightener

Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-stryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(stryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-stryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbly chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li)

phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

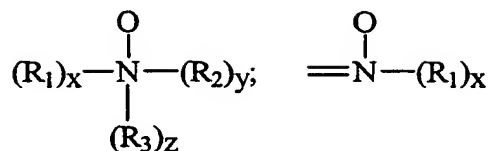
Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process.

Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x , y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $\text{pK}_a < 10$, preferably $\text{pK}_a < 7$, more preferred $\text{pK}_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

Optical Brighteners

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) and percarbonate bleaches can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent

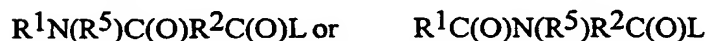
Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:



wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam,

nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Anti-Static Agents

The present compositions can also comprise anti-static agents as illustrated in U.S. Pat. 4,861,502. Preferred examples of anti-static agents include alkyl amine-anionic surfactant ion pairs, such as distearyl amine-cumene sulfonate ion pairs. If present, anti-static agents are present in an amount of from about 0.5% to about 20%, preferably from about 1% to about 10%, more preferably from about 1% to about 5%, by weight of the detergent composition.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

| | | |
|--------|---|--|
| LAS | : | Sodium linear C ₁₁₋₁₃ alkyl benzene sulfonate |
| TAS | : | Sodium tallow alkyl sulfate |
| CxyAS | : | Sodium C _{1x} - C _{1y} alkyl sulfate |
| C46SAS | : | Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate |

| | | |
|-------------|---|--|
| CxyEzS | : | Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide |
| CxyEz | : | C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide |
| QAS | : | R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄ |
| QAS 1 | : | R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ - C ₁₁ |
| APA | : | C ₈ - C ₁₀ amido propyl dimethyl amine |
| Soap | : | Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids |
| STS | : | Sodium toluene sulphonate |
| CFAA | : | C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide |
| TFAA | : | C ₁₆ -C ₁₈ alkyl N-methyl glucamide |
| TPKFA | : | C ₁₂ -C ₁₄ topped whole cut fatty acids |
| STPP | : | Anhydrous sodium tripolyphosphate |
| TSPP | : | Tetrasodium pyrophosphate |
| Zeolite A | : | Hydrated sodium aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ .27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis) |
| NaSKS-6 | : | Crystalline layered silicate of formula δ- Na ₂ Si ₂ O ₅ |
| Citric acid | : | Anhydrous citric acid |
| Borate | : | Sodium borate |
| Carbonate | : | Anhydrous sodium carbonate with a particle size between 200μm and 900μm |
| Bicarbonate | : | Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm |
| Silicate | : | Amorphous sodium silicate (SiO ₂ :Na ₂ O = 2.0:1) |
| Sulfate | : | Anhydrous sodium sulfate |
| Mg sulfate | : | Anhydrous magnesium sulfate |
| Citrate | : | Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm |
| MA/AA | : | Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000 |

| | | |
|-----------------|---|--|
| MA/AA (1) | : | Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000 |
| AA | : | Sodium polyacrylate polymer of average molecular weight 4,500 |
| CMC | : | Sodium carboxymethyl cellulose |
| Cellulose ether | : | Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals |
| Protease | : | Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase |
| Protease I | : | Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc. |
| Alcalase | : | Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S |
| Cellulase | : | Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme |
| Amylase | : | Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T |
| Lipase | : | Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase |
| Lipase (1) | : | Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra |
| Endolase | : | Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S |
| PB4 | : | Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ |
| PB1 | : | Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ |
| Percarbonate | : | Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ |
| NOBS | : | Nonanoyloxybenzene sulfonate in the form of the sodium salt |
| NAC-OBS | : | (6-nonamidocaproyl) oxybenzene sulfonate |
| TAED | : | Tetraacetythylenediamine |

| | | |
|----------------|---|--|
| DTPA | : | Diethylene triamine pentaacetic acid |
| DTPMP | : | Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060 |
| EDDS | : | Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt. |
| Photoactivated | : | Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin soluble polymer |
| Photoactivated | : | Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin soluble polymer |
| Brightener 1 | : | Disodium 4,4'-bis(2-sulphostyryl)biphenyl |
| Brightener 2 | : | Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate |
| HEDP | : | 1,1-hydroxyethane diphosphonic acid |
| PEGx | : | Polyethylene glycol, with a molecular weight of x (typically 4,000) |
| PEO | : | Polyethylene oxide, with an average molecular weight of 50,000 |
| TEPAE | : | Tetraethylenepentaamine ethoxylate |
| PVI | : | Polyvinyl imidosole, with an average molecular weight of 20,000 |
| PVP | : | Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000 |
| PVNO | : | Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000 |
| PVPVI | : | Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000 |
| QEA | : | bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30 |
| SRP 1 | : | Anionically end capped poly esters |
| SRP 2 | : | Diethoxylated poly (1, 2 propylene terephthalate) short block polymer |

- PEI : Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
- Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
- Opacifier : Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
- Wax : Paraffin wax

In the following examples all levels are quoted as % by weight of the composition:

Example 1

In this example 400 grams of activated zeolite X is placed in a high pressure vessel. The vessel is evacuated. The vessel is then charged with CO₂ at a pressure of 10 barg. This pressure is maintained for 10 minutes. The pressure is then released and the CO₂ loaded zeolite is removed and stored in a glass jar.

Upon addition of the 10 grams of the CO₂ loaded zeolite to a beaker of water there is rapid release of the CO₂ to produce bubbles, and the evolution of significant localized heat.

Example 2

The following laundry detergent compositions A to F are prepared and 10 % by weight of material prepared in example 1 is added to each of the formulations. Upon addition to of each of the resulting formulations to water, gas bubbles are observed in accordance with the invention.

| | A | B | C | D | E | F |
|----------|-----|-----|-----|-----|-----|-----|
| LAS | 8.0 | 8.0 | 8.0 | 2.0 | 6.0 | 6.0 |
| TAS | - | 0.5 | - | 0.5 | 1.0 | 0.1 |
| C46(S)AS | 2.0 | 2.5 | - | - | - | - |
| C25AS | - | - | - | 7.0 | 4.5 | 5.5 |
| C68AS | 2.0 | 5.0 | 7.0 | - | - | - |

| | | | | | | |
|-------------|------|------|------|------|------|------|
| C25E5 | - | - | 3.4 | 10.0 | 4.6 | 4.6 |
| C25E7 | 3.4 | 3.4 | 1.0 | - | - | - |
| C25E3S | - | - | - | 2.0 | 5.0 | 4.5 |
| QAS | - | 0.8 | - | - | - | - |
| QAS (I) | - | - | - | 0.8 | 0.5 | 1.0 |
| Zeolite A | 18.1 | 18.0 | 14.1 | 18.1 | 20.0 | 18.1 |
| Citric acid | - | - | - | 2.5 | - | 2.5 |
| Carbonate | 13.0 | 13.0 | 27.0 | 10.0 | 10.0 | 13.0 |
| SKS-6 | - | - | - | 10.0 | - | 10.0 |
| Silicate | 1.4 | 1.4 | 3.0 | 0.3 | 0.5 | 0.3 |
| Citrate | - | 1.0 | - | 3.0 | - | - |
| Sulfate | 26.1 | 26.1 | 26.1 | 6.0 | - | - |
| Mg sulfate | 0.3 | - | - | 0.2 | - | 0.2 |
| MA/AA | 0.3 | 0.3 | 0.3 | 4.0 | 1.0 | 1.0 |
| CMC | 0.2 | 0.2 | 0.2 | 0.2 | 0.4 | 0.4 |
| PB4 | 9.0 | 9.0 | 5.0 | - | - | - |

| | | | | | | |
|--------------------------------|--------|--------|--------|------|--------|--------|
| Percarbonate | - | - | - | - | 18.0 | 18.0 |
| 1TAED | 1.5 | 0.4 | 1.5 | - | 3.9 | 4.2 |
| NAC-OBS | - | 2.0 | 1.0 | - | - | - |
| DTPMP | 0.25 | 0.25 | 0.25 | 0.25 | - | - |
| SRP I | - | - | - | 0.2 | - | 0.2 |
| EDDS | - | 0.25 | 0.4 | - | 0.5 | 0.5 |
| CFAA | - | 1.0 | - | 2.0 | - | - |
| HEDP | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 |
| 1QEA | - | - | - | 0.2 | - | 0.5 |
| Protease I | - | - | 0.26 | 1.0 | - | - |
| Protease | 0.26 | 0.26 | - | - | 1.5 | 1.0 |
| Cellulase | 0.3 | - | - | 0.3 | 0.3 | 0.3 |
| Amylase | 0.1 | 0.1 | 0.1 | 0.4 | 0.5 | 0.5 |
| Lipase (1) | 0.3 | - | - | 0.5 | 0.5 | 0.5 |
| Photoactivated bleach (ppm) | 15 ppm | 15 ppm | 15 ppm | - | 20 ppm | 20 ppm |

| | | | | | | |
|---------------------|------|------|------|-----|------|------|
| PVNO/PVPVI | - | - | - | 0.1 | - | - |
| Brightener 1 | 0.09 | 0.09 | 0.09 | - | 0.09 | 0.09 |
| Perfume | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.4 |
| Silicone antifoam | 0.5 | 0.5 | 0.5 | - | 0.3 | 0.3 |
| Misc/minors to 100% | | | | | | |
| Density in g/litre | 850 | 850 | 850 | 850 | 850 | 850 |

Accordingly, having thus described the invention in detail, it will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.